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HYDROCHLORIC ACID LEACH OF AN ELLIOT LAKE URANIUM PRECONCENTRATE

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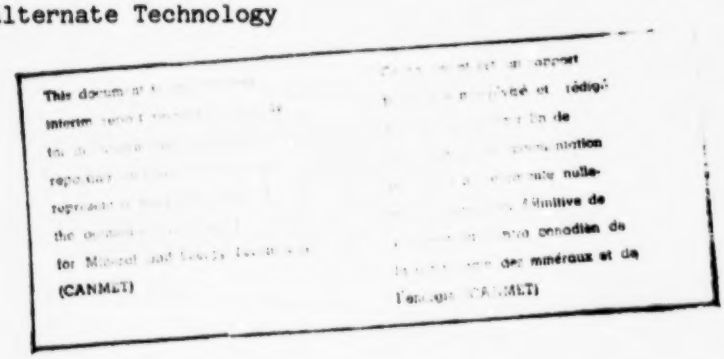

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by

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ABSTRACT

Hydrochloric acid leaches were conducted on the radioactive concentrate obtained from an Elliot Lake uranium ore by flotation and high intensity magnetic separation. Suitable leach conditions were obtained from bench-scale leach tests. The best first stage leach residue contained U-0.008%, Th-0.017% and Ra(226) 94 pCi/g solids. This uranium level is fairly high with respect to the uranium level of the current Elliot Lake uranium mill tailings (i.e., 0.0060%). As a result, second stage hydrochloric acid leaches were conducted and the residue obtained was found to contain U-0.003%, Th-0.011% and Ra(226) 46 pCi/g solids.

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INTRODUCTION

Elliot Lake of Ontario is a major uranium-producing area in Canada. The principal uranium-bearing minerals are brannerite and uraninite, present in the quartz-pebble conglomerates (1,2). The uranium grade of the ore is in the range of 0.08-0.12%. Pyrite is also present in the ore and averages to 6.5%.

Sulphuric acid is the most common reagent employed to process the uranium ore. In fact, sulphuric acid solubilizes 94-96% uranium leaving behind almost all of the radium in the solid effluent. This solid effluent finally reports to the disposal sites. Again, pyrite which is sparingly soluble in sulphuric acid also ends up in the same disposal sites.

Some components (e.g., sulphides) of the tailings in the disposal site undergo oxidative dissolution both by chemical and biochemical means. Biochemically, certain bacteria such as thiobacillus ferro-oxidans and thiobacillus thio-oxidans which commonly occur in the disposal sites initiate the oxidation of sulphide minerals (3). For example, pyrite undergoes bacterial oxidation giving rise to ferric ion and sulphuric acid (Eq 1). Ferric ion also reacts

$$2\ FeS_2 + 2H_2O + 15/2\ O_2 \rightleftharpoons Fe_2(SO_4)_3 + H_2SO_4 + H_2O \qquad \text{Eq 1}$$

with pyrite yielding ferrous ion (Eq. 2). Furthermore,

$$FeS_2 + 7\ Fe_2(SO_4)_3 + 8\ H_2O \rightleftharpoons 15\ Fe\ SO_4 + 8\ H_2SO_4 \qquad \text{Eq 2}$$

both ferric ion and sulphuric acid are effective leachants to solubilize other heavy metal components (e.g. Zn, Cn, Ni, Co, Ti, Fe, Mn, etc.). As a result, these tailing sites become the centre of great environmental concern.

Because of current environmental concern over the issue of uranium mine mill effluents CANMET (Canada Centre for Mineral and Energy Technology) is particularly interested in the evaluation of alternative processing technology for the uranium ore. A new process must not only be suitable to yield more environmentally acceptable tailings but also be economically viable (4).

To this end various processing options have been considered, such as nitric acid and hydrochloric acid leachings of the whole ore or of the pre-concentrates (6). Alternatively, acid chloride (i.e. HCl) or salt chloride (e.g. NaCl or HCl) leaches could be conducted on the sulphide and on the radioactive mineral concentrates separated from the conventional sulphuric acid leach tailings by flotation and high intensity magnetic separation technique (7,8).

Recently, it has been demonstrated that hydrochloric acid leaching of the Elliot Lake uranium ore can actually yield tailings containing 20-25 pCi/g radium/g solids with essentially all the pyrite remaining in the tailings (6). This type of tailing would eliminate much of the concern over radium(226) but acid generation by pyrite oxidation would continue. Therefore, HCl leaching of pyrite free uranium concentrate might yield tailings free of concerns not only over radium(226) issue but also over acid generation by pyrite oxidation.

This report describes the results of hydrochloric acid leaching of pyrite free uranium concentrate.

GENERAL PROCEDURE

The Mineral Processing Laboratory of CANMET supplied the radioactive mineral concentrate. The radioactive mineral concentrate which represents approximately 20% of the total weight of the uranium ore and 60% of U, 67.4% of Th and 56% of Ra* was separated from the uranium ore supplied by Rio Algom Limited, Elliot Lake, Ontario by the combination of flotation and high intensity magnetic separation techniques (8). Table 1 shows the screen analysis which indicates that more than 54% of the particles were under 200 mesh size and Table 2 shows the partial chemical analysis of the radioactive mineral concentrate, and the uranium ore employed for the concentration of radioactive minerals by flotation and high intensity magnetic separation. It is assumed from sulphur value (Table 2) that approximately 1% pyrite is still present in the radioactive mineral concentrate.

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*Remaining per cents of U, Th and Ra are distributed in the pyrite concentration and flotation tail.

Table 1 - Particle size distribution

Screen size (mesh)	% wt retained
+28	10.0
-100	7.2
-150	23.8
-200	1.9
270	2.9
-325	49.7

Table 2 - Partial chemical analysis (wt %)

Elements	Radioactive Min. Conc	Uranium Ore*
Uranium	0.20	0.080
Thorium	0.085	0.038
Radium (266)	720 pCi/g	280 pCi/g
Iron	2.40	3.12
Calcium	0.18	0.14
Aluminum	6.14	3.62
Magnesium	0.20	0.12
Sulphur (total)	0.46	2.97
Silicon	39.4	38.39

*Feed for flotation and high intensity magnetic separation

The required volume of water and hydrochloric acid of 37 wt % concentration were added to a weighed sample of uranium concentrate, so that the desired acid concentration and pulp density were maintained. When the temperature reached the desired level, sodium chlorate was added in the scale of 2.5 kg $NaClO_3$/tonne of concentrate. The leach slurry was kept agitating for the duration of leaching. Acidity (i.e., pH) and the oxidation potential (i.e., EMF) of the leach slurry were monitored at intervals. At the end of leaching the leach slurry was filtered under vacuum and the residue was washed twice with water acidified with 1 vol % HCl and once with water. All the washings were carried out with approximate solid to liquid ratio of 1:1.

The feed sample for the second stage leaching was obtained by mixing thoroughly a number of first stage leach residues. All the second stage leaches were conducted with 44.0/kg HCl/tonne on a leach slurry containing 50% solids. Combined filtrates and the dried residues were analyzed.

Unless otherwise mentioned, the radium assay indicates radium (226) isotope only.

RESULTS AND DISCUSSION

Temperature Effect

A set of leaches was conducted at 25, 50, 70, 85 and 95°C but at constant retention time (24 h), acid concentration (44.0 HCl kg/tonne) and pulp density (50% solids). Figure 1 shows the extractions of uranium, thorium, and radium as a function of temperature.

The curves of Fig. 1 indicate that the per cent extractions of uranium increased steadily with the increase in the leach temperature. As a result the highest per cent of uranium extraction (96%) appeared at 95°C which is the highest temperature applied in this set of leaches. Regarding temperature effect on the extraction of thorium and radium similar phenomenon is also observed but only up to 70°C. In fact the highest per cent extractions of thorium (78%) and of radium (82%) respectively occured at 70°C; however their extractions started to decline with further increase in temperature.

The chemical analysis of the leach liquors indicates that approximately 60% of 0.76% sulphur of the feed (Table 2) went into solution at 95°C in contrast to 20% sulphur at 25°C. Obviously, the decline in radium extraction could be due to formation of insoluble $RaSO_4$. Most likely, at 70°C the

concentration of sulphate reached the critical stage when $RaSO_4$ formation became more prominent than the solubilization of $RaSO_4$. Unlike radium, thorium extraction suffered a great deal more at temperatures above 70°C. At present it is not possible to put forward any rational explanation for such an effect on thorium extraction.

It is also evident in Fig. 1 that 94% uranium extraction took place at 70°C. In view of the confidence limit of uranium determination by fluorometry (1-0.05%; private communication - L. Dalton, MSL, 1982) it may be assumed that the per cent of uranium extraction remained virtually constant from 70-95°C. Therefore, 70°C would be the optimum leach temperature.

Retention time effect

To find a suitable retention time for the highest per cent extractions of uranium, thorium and radium a series of leaches was conducted with 6, 16, 24, 36 and 48 hours retention time but at constant temperature of 70°C, acid concentration of 44.0 kg HCl/tonne and pulp density of 50% solids. Figure 2 shows uranium, thorium and radium extraction as a function of retention time.

It is evident in Fig. 2 that radium extraction is not sensitive to the variation of retention time. In fact its highest per cent extraction, 82%, appeared after 6 hours of leaching and remained unchanged up to 48 hours of retention time which is the longest retention time applied in this set of leaching. Similarly uranium extraction essentially remained constant at an average level of 94% from 6 to 48 hours of retention time. However, unlike uranium and radium, thorium extraction rate started to increase after 16 hours of leaching and its highest per cent extraction (86%) appeared after 48 hours of retention time.

Since the shorter retention time is more economical than the longer one and also the economy of the uranium ore processing depends on the efficient extraction of uranium, therefore, 6 hours leaching can be considered as the optimum retention time.

Effect of acid concentration

A series of leaches was conducted with varying concentration of hydrochloric acid while the temperature, retention time and the pulp density were kept constant at 70°C, 24 hours and 50% solids respectively. Figure 3

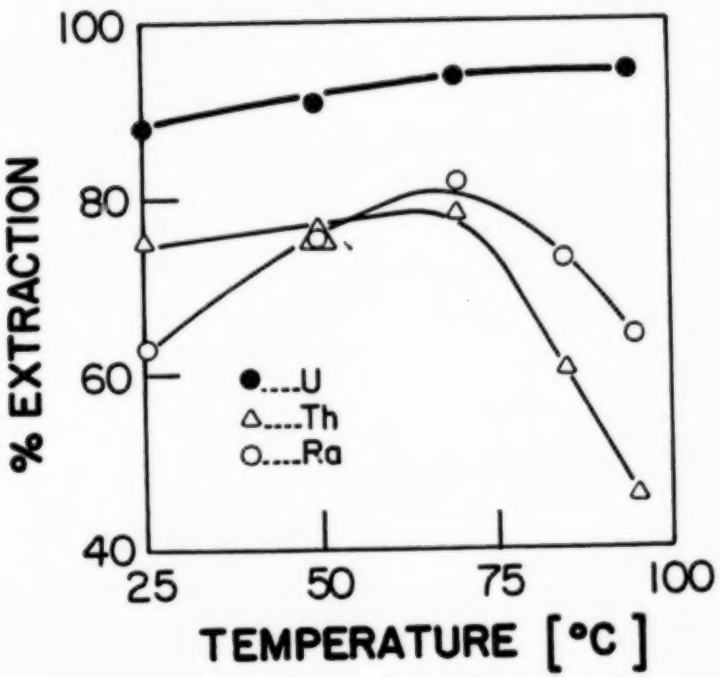

Fig. 1 - Uranium, thorium and radium extractions as a function of temperature

shows extractions of uranium, thorium and radium as a function of acid concentration.

It is evident from this figure that the extractions of uranium, thorium and radium increased as the concentrations of hydrochloric acid were increased. However, the highest per cent extractions of uranium 97%, thorium 80% and radium 87% occured with 66.0 kg HCl/tonne. Obviously, these data lead to the conclusion that 66.0 kg HCl/tonne of concentrate would be the suitable acid concentration.

Effect of pulp density

To study the effect of pulp density a set of leaches was conducted with varying concentration of solids in the leach pulp while the temperature, retention time and acid concentration were kept constant at 70°C, 24 hours and 44.0 kg HCl/tonne respectively. Figure 4 represents uranium, thorium and radium extractions as a function of pulp density.

It is evident in Fig. 4 that uranium and radium extraction are not significantly affected with the variation of the concentration of solids in the leach slurry. As a matter of fact uranium and radium extractions remained at average levels of 94% and 78% respectively throughout the range of pulp density variation applied in this set of leaches. Thorium extraction, which increased with the increase of solids in the leach slurry, reached its highest level (78%) when the leach slurry contained only 50% solids. Therefore, these experimental observations lead to the conclusion that 50% solids in the leach slurry would be the optimum pulp density.

SECOND STAGE LEACHING

The data of Table 3 indicate that the radionuclides level in the best residue from the first stage leaches are fairly high. The uranium level is higher than usually present in the Elliot Lake uranium mill tailings (i.e., 0.006% U) (13). In order to further reduce the radionuclides level HCl leaches were conducted on the first stage leach residue. Table 4 represents radionuclides level of the second stage leach residue. In fact, the second stage leach residue contains less uranium than the current Elliot Lake uranium mill tailings. If for any reason further reduction in the radium level is required the following measure may be taken.

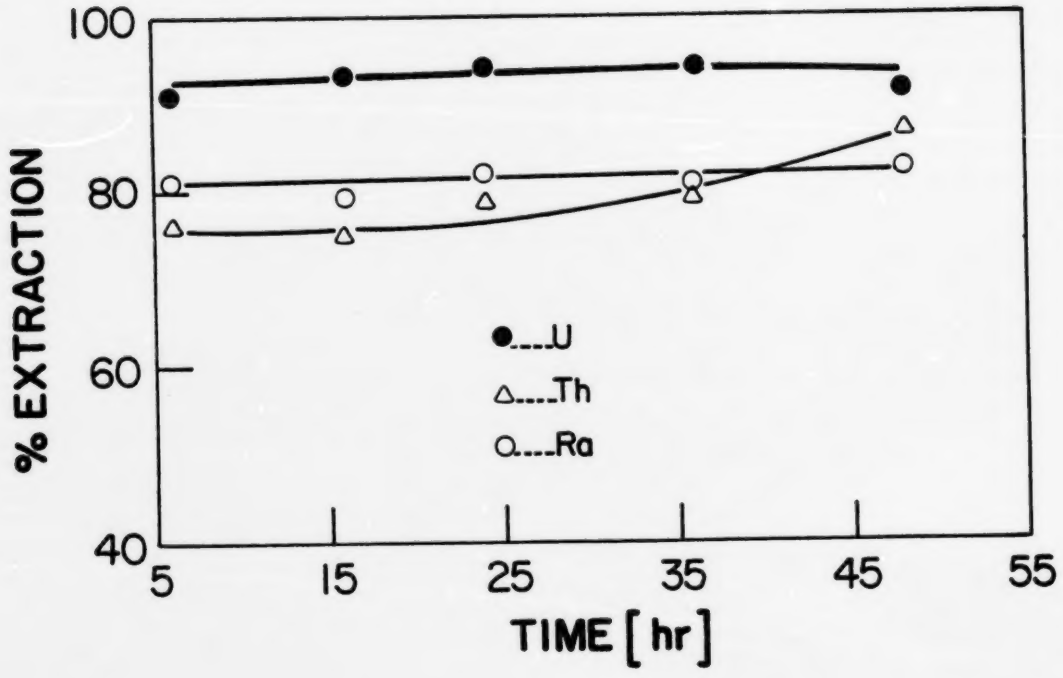

Fig. 2 - Uranium, thorium and radium extractions as a function of retention time

Radioactive equilibrium predicts that approximately 10-11 pCi/Ra226/g solids would be present in the second stage leach residues (11). Radium in excess of 11 pCi/g must be in the form of insoluble salt or salts. These insoluble salts (e.g., $RaSO_4$) may be solubilized by treatment with salt chloride (e.g., NaCl, KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$). Various researchers have demonstrated that salt chlorides, particularly of alkali or alkaline earth metals, are effective in solubilizing radium sulphate present in the conventional sulphuric acid leach tailings (10,11,12,14). However, this type of study will be conducted at some future date.

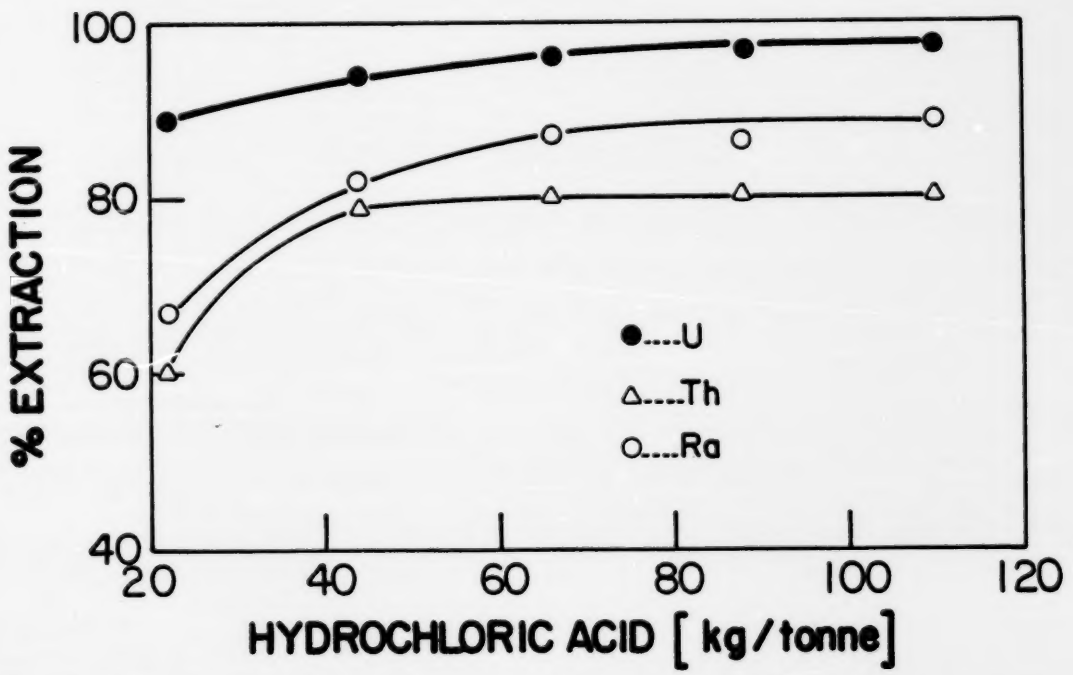

Fig. 3 - Uranium, thorium and radium extractions as a function of acid concentration

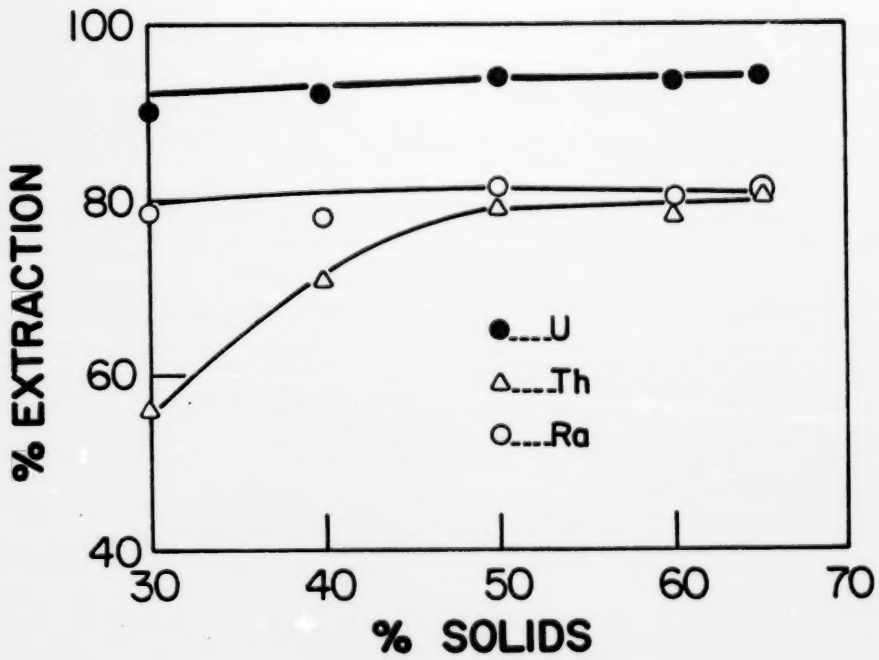

Fig. 4 - Uranium, thorium and radium extraction as a function of pulp density

Table 3 - Leach conditions and the analyses of the best residue

Temp (°C)	Time (h)	HCl (kg/t)	Pulp density (% solids)	U (wt %)			Th (wt %)			Ra(226) (pCi/g)		
				Feed	Residue	Extraction	Feed	Residue	Extraction	Feed	Residue	Extraction
70	6	66.0	50	0.2	0.008	96%	0.085	0.017	81%	720	94	87%

Table 4 - Radionuclides level of the second stage leach residue and overall extraction*

Temp (°C)	Time (h)	HCl (kg/t)	Pulp density (% solids)	U (wt %)			Th (wt %)			Ra(226) (pCi/g)		
				Feed	Residue	Overall Extraction	Feed	Residue	Overall Extraction	Feed	Residue	Overall Extraction
70	6	44.0	50	0.015	0.003	98.5%	0.024	0.011	87.0%	160	46	94%

*Leach conditions were not optimized; a mixture of several 1st stage leach residues served as feed. Overall extraction figures represent only from the radioactive mineral concentrate.

CONCLUSION AND RECOMMENDATION

Optimum leach conditions of temperature 70°C, retention time 6 hours, acid contentration-66.0 kg HCl/tonne and pulp density-50% solids for hydrochloric acid leaching of the preconcentrate of Rio Algom uranium ore were obtained.

The first stage leach residue contained U-0.008%, Th-0.017% and Ra 94 pCi/g solids. In fact uranium level of this residue is higher than that of the current Elliot Lake uranium mill tailings (i.e., ~0.0060% U).

The second stage HCl leachings reduced the radionuclides level considerably and yielded residue containing U-0.003%, Th-0.011% and Ra-46 pCi/g solids. The overall uranium thorium and radium extractions appear to be 98-5%, 87% and 94% respectively.

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